Photoinduced Collision Processes of Metastable Hydrogen Atoms
with H_2 in the Energy Range 0.05 - 0.47eV.

F.J. Comes and U. Wennig

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Atoms with H_2 in the Energy Range 0.05 -0.47 eV

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Molecular hydrogen was excited by selective ab-

sorption of ultraviolet radiation of appropriate

wavelength into the vibrational levels v' =3,

4, and 5 of the electronic D ($^1\pi$u)-state. For

the radiation bandwidth chosen the molecule was

only formed in the rotational levels J = 1 and

2 of the R-branch. The excited molecules decay

by predissociation into two hydrogen atoms of

translational energy which is equal to one half

of the difference between the excitation and dis-

sociation energies. One of the atoms is formed

in the first excited state. The formation of

the excited species can be proven by its fluo-

rescence (Lyman$_\alpha$-radiation).

As a result the measurements show, that the

excited atoms are all in the metastable 2S-state

and not in the short-lived 2P-state.   Without

electric fields these metastable atoms loose their

excitation energy in collision with the surrounding

hydrogen molecules. One part (a) follows an in-

duced transition to the electronic ground state

by the emission of Ly_α-radiation (1216Å), the

other part (b) is transformed to products or under-

goes an energy transfer process without emitting

Ly_α-radiation.

If a quenching field is applied spontaneous

emission will compete with collisional deacti-

vation, which allows the deactivation cross sec-

tions to be calculated. These cross sections are

between 50 and 100 $\overset{\circ}{A}{}^2$ (a) and about 50 $\overset{\circ}{A}{}^2$ in case

(b). In case (a) the collision cross section in-

creases with the velocity of the particles where-

as in case (b) a constant value was found.

The investigation of the fine-structure of the hydrogen

atom in the state n=2 by means of high-frequency spectroscopy

led about twenty years ago to the discovery of the Lamb-shift.

This and subsequent experiments were aimed at measuring the

level differences:

$$2S_{1/2} - 2P_{1/2} \quad \underline{viz}. \quad 2P_{3/2} - 2S_{1/2}$$

The metastable state $2S_{1/2}$ agrees with these measurements very well since a transition to these two P-states is permitted by light radiation. The probability of spontaneous transitions is very small, however, because of the small level spacing. Under suitable conditions induced transitions can be brought about. In order to avoid collision processes which can lead to a change in the occupation density in the observed atomic states, the experiments were carried out with atomic beams.

In order to study the reactability of excited H-atoms, however, collision experiments must be carried out. This can be done with the method of crossed molecular beams - this procedure can be used, because of the necessary distance between place of origen and place of reaction, only for metastable or highly excited atoms which possess a long life - , or photo-chemical experiments can be performed in which, on the basis of rather high particle density, collisions are possible within the life of even short-lived, excited particles.

1.)

W. E. Lamb, Jr. u. R. C. Retherford, Phys. Rev. 79, 549 [1950].

- R. T. Robiscoe, Phys. Rev. 138, A22 [1965] - R. T. Robiscoe u. B. L. Cosens, Phys. Rev. Let. 17, 69 [1966].

Recently from the field of spectroscopic study, a further method of investigating the reactivity of especially metastable hydrogen atoms was found. [2] By the absorption of ultraviolet light in the radiation bandwidths of the S ($^1\pi$ u)-state of the hydrogen molecule, the molecule is dissociated predominately above the limit of ionization. With this dissociation excited hydrogen atoms are produced. The behavior of the excited atoms can be observed by measuring their fluorescence (Ly$_\alpha$ - radiation).

The photo dissociation at the dissociation limit is explained as a pre-dissociation of the D-X (3.0) levels. Namioka assumed the following scheme of decay: [3]

$$H_2 \ (D^1\pi_u \ v' \geqq 3) \to H_2 \ (B'^1\Sigma^+_u), \tag{1}$$

$$H_2 \ (B'\Sigma^+_u) \to H \ (1S, \ 2P) + E_{kin}$$
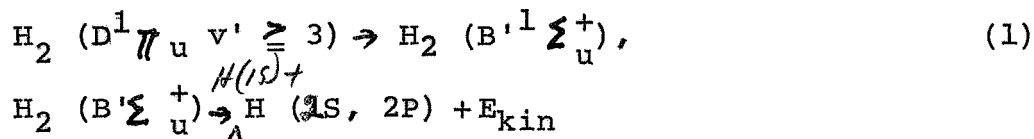
Most recently the photo-ionization of hydrogen has also undergone a renewed investigation. While Beutler and Jünger [4] calculated the ionization limit from the auto-ionization of the

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2.)
   F. J. Comes u. H. O. Wellern, Z. Naturforsch, 23a 881 [1968]-

   F. J. Comes, B. Schmitz, H.O. Wellern u. U. Wenning. Ber.

   Bunsenges.Phys. Chem. 72 986 [1968]

3.)
   T. Namioka, J. Chem. Phys. 41, 2141 1964; ibid.43. 1436 [1965]

4.)
   H. Beutler u. H.O. Jünger, Z. Phys. 100, 80 [1936]

higher rotational levels of the D-X (6.0) band, Chupka in

particular was able to show that the rotation level R(1) of

this band leads to ionization. [5.] Thus a new value resul-

ted for the ionization potential. Both from the measurements

of Chupka and from our own measurements, which were carried [6.]

out with the resolvability of $\lambda/\Delta\lambda > 10^4$, it is clear that in

the vicinity of the ionization limit, the formation of ions

takes place mainly through auto-ionization from the highly

excited neutral states and not through a direct transition

from the ground state into the ionization contiuum.

The hydrogen atoms which were excited by the photodissocia-

tion are found in the metastable state, as will be demonstrated

in the course of this work. The hydrogen atoms have a kinetic

energy which equals half the difference between the molecular

excitation and the dissociation energy of the $B(1\Sigma_u^+)$-state.

Since the latter is known with exactness and the former can

be found from measurements, the kinetic energy of the hydrogen

atoms can be calculated. Therefore, through the absorption of

ultraviolet light in the well-known D-bands of the hydrogen

molecule, "hot" hydrogen atoms with definable kinetic energy

can be produced. In an earlier work we were able to show that

these atoms, at least in part, are in the metastable 2S-state.

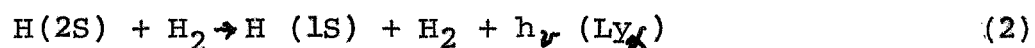Collision processes with atoms in the ground state as well as

5.)
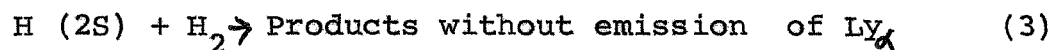   W. A. Chupka u. J. Berkowitz, J. Chem. Phys. 48 5726 [1968].

  6.)
    F. J. Comes u. B. Schmitz, Z. Naturforsch (In Vor-
    bereitung).

in excited states are of great interest to reaction kinetics. They are also of significance in the discussion of processes in the higher atmosphere of our earth and the atmospheres of other planets.

The present paper deals with the origin of metastable hydrogen atoms through photo-dissociation and their deactivation in collision processes. Through the choice of the excitation energy and the application of a homogeneous electrical field in the collision region, the kinetic energy and the life span of the metastable hydrogen atoms can be predicted exactly and can be changed commensurably. Thus, from the experiments both the branching ratio during the dissociation into the atomic states 2S and 2P and the average impulse and its energy output for the processes

$$H(2S) + H_2 \rightarrow H(1S) + H_2 + h_\nu (Ly_\alpha) \tag{2}$$

and

$$H(2S) + H_2 \rightarrow \text{Products without emission of } Ly_\alpha \tag{3}$$

can be calculated.

Experiment

For the measurement of hydrogen absorption and atom fluorescence, an apparatus was used which in principle has been described elsewhere.[2.)] Also, in the present experiments the Hopfield Continuum was used to excite the hydrogen spectrum. The entire apparatus has, however, been greatly

improved, the result of which is considerably greater sensitivity. Through the improvement of the monochromator adjustment, the affective cross section of absorption and the photoionization of the hydrogen molecule could be measured with a resolving factor of $\sim 10^4$. The increase in signal-noise relationship of the Ly_α detector increased the detection sensitivity by more than an order of magnitude over the earlier system. Thus it was possible to determine from the Ly_α-radiation the competition between collisions of the metastable atoms with H_2-molecules and their spontaneous emission. The high resolvability was attained by a measurement in the third order of the light-source spectrum, which was produced by a grid with 1200 lines/mm and a 1 m radius. The aperture widths at entrance and exit of the monocromator were 18μ.

The ultraviolet intensity at the exit aperture was in the order of 10^6 quanta per sec. In order to be able to perform measurements while using this small light intensity, the light source was stabilized electronically. That not only resulted in a very high emission stability but it also lowered considerably the measurable electrical disturbance. Only because of the high stability of the primary stimulus were we able to differentiate commensurably well between fluorescence signals of less than 10 impulses per minute and the background signals (1-2 impulses per minute.) The maximal impulse rate

at the input of the counter equalled 10 impulses per second.

Figure 1 shows the block diagram of the light source re-
gulator. By means of an impulse generator, a thyratron cir-
cuit is activated which regulates the charging and discharging
of the condensor (3000 p F) lying parallel to the light source.
In this way the time of discharge and the repetition frequen-
cy could be controlled exactly. With a maximum voltage of 6kV,
the light source is usually operated at a frequency of 15 kc,
in order to keep the acoustic signal out of the range of
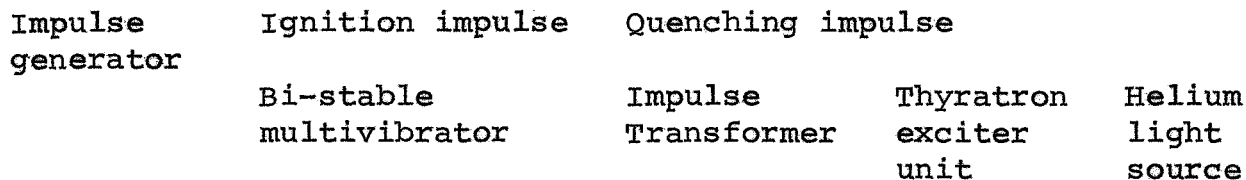normal hearing.

(Diagram)

Impulse   Ignition impulse   Quenching impulse
generator

        Bi-stable   Impulse   Thyratron   Helium
        multivibrator   Transformer   exciter   light
                                        unit   source

Figure 1. Block diagram of the light source regulator.

The light signals from the fluorscent chamber were ob-
served vertically to the primary light direction. As Ly_α-detec-
tor an open Bendix secondary electron multiplier with a tungsten
cathode and a Li F window as short wave filter were used. Thus
the limit of measurement was kept within a wave length interval
of 1050-1500 Å. By using a Ca F_2 window, the interval could
be narrowed to 1230-1500 Å so that the Ly_α-radiation was su-
pressed. Although no further filters, as for example a O_2-
absorption space, were used in connection with the usual mea-
suring devices, the light emission could be identified positively

as Ly_α-radiation. The measuring method for this is discussed in the next chapter.

The pressure determination of hydrogen in the measuring chamber was done with a McLeod manometer. For the ambient sur- veilance of pressure stability, a thermoelectric vacuum meter was used. With an ionization manometer the residue gas pres- sure in the apparatus without hydrogen could be checked. The H_2-pressure lay between 8 and 30 x 10^{-3} Torr.

Making the Measurements

The measuring chamber is so constructed that effective cross section of absorption, ionization and fluorescence can be observed simultaneously. Actually, only two values were measured at the same time, either those of absorption and ionization or those of absorption and fluorescence. The coupling of ion measurement, or, as the case might be, fluo- rescence measurement with the measurement of absorption served to produce an exact spectral arrangement of the individual measurements. In the following, however, only the measurements of fluorescence are discussed. A discussion of the measured absorption and ionization cross section will take place later. [6)]
While the absorption, viz. the ionization cross sections, were obtained for the exact identification of the molecular states with a line width of 0.08Å, the atomic fluorescence, for rea- sons of intensity, was obtained with a line width of 0.2Å. According to information in the highly-resolved absorption

spectrum, the individual vibration states of the D-band can be
excited at this resolution individually. However, the rota-
tion levels J=1 and J=2 are activated simultaneously. At
room temperature the ground state for J=1 is saturated.
Since predissociation begins in the third and ionization be-
gins in the sixth vibration bands, the fluorescence observa-
tions were made primarily in the vibrational bands v' = 3,
4, and 5. The kinetic energy of the H-atoms from the disso-
ciation process with absorption in the three bands is in each
case 0.052 eV, 0.167 eV and 0.272 eV.

The measured values for atomic fluorescence, which lie as
the basis of this work, are the results of numerical measure-
ments. The individual value is the numerical rate per minute
calculated for a period of 2-5 minutes. The final values
upon which the later measurement curves are based, are average
values taken from a large number of individual measurements.
In order to utilize the counting periods of the given quan-
tity effectively, the variation in light source emission
must be smaller than the statistical error of the measured
values. These variations were smaller than 2% per hour.

The L_α - fluorescence of the H-atoms was measured in the
measuring chamber at a constant H_2-pressure. Since mesta-
table H-atoms in the electrical field are quenchable - their
life span is inversely proportional to the square of the field

strength - through the measurement of the atomic fluorescence
as function of field strangth, the impulse deactivation of the
particles excited to their metastable state can be investiga-
ted. With sufficiently high field strength , the collision
of the excited particles can be avoided entirely, because then
the particles, because of their greatly shortened life span
lose their excitation energy through spontaneous emission.

Two different systems were used to determine the atomic
fluorescence. In the first case, the Ly_α -detector was made
vertical to the field direction, in the second case, parallel
to the direction of the quenching field. With this, the in-
fluence of the detector field on the quenching of the metastable
atoms could be studied. The field was produced between two para-
llel plates, viz. very transparent grids of sufficient dimen-
sions, so that in the vicinity of the primary beam a sufficient-
ly homogeneous field could be assured. With observation ver-
tical to the field direction, the field-dependent increase in
measurable radiation was smaller than in the second method of
observation. This effect could be definitely established to be
quenching by the penetrating multiplier field. Through this,
even without applied measuring chamber voltage, H-atoms are
quenched. That lessens the possible increase in fluorescence
at complete quenching by the electrical field. In order to
compensate for the penetration of the multiplier field, the
measuring cell, for the attainment of maximum results with

observations parallel to the field, had to be placed under a potential of about 14 volts.

It was essential to identify the measured radiation as Ly_α-emission. Even with earlier measurements it had been necessary to know that we were dealing with Ly_α-radiation [2.)] in connection with the fluorescence of hydrogen when ultra-violet light in the higher vibration levels of the D-state is absorbed. Important evidence was the value of the measured absorption coefficients for the fluorescence radiation through molecular oxyden [7.)], the additivity of ionization and fluorescence to the total absorption in the D-bands, the spectral progress of absorption and fluorescence in the region between the ionization and dissociation limit and the quenchability of radiation in the electrical field. [2)] In the present case it can be proved clearly that with this radiation it is a question only of fluorescence of the metastable H-atoms.

In Figure 2 the measured fluorescence is given as a function of the field strength of the electrical quenching field for the absorption in the three various vibration levels of the molecular D-state. The intensity of the radiation is dependent upon the field strength, which is only possible with metastable H-atoms. As discussed under Discussion of Measurements,

7.)
    K.D. Beyer u. K.H. Welge, Z. Naturforsch 22a, 1161 [1967].

one can show that an optimal adjustment of the calculated curve

to the measured values is only then possible when the total

radiation comes exclusively from metastable atoms. With the

observation of fluorescence vertical and parallel to the elec-

trical field, in each case two different plate positions were

used. After adjusting the quenching process by means of the

multiplier field for the observation vertical to the field,

one can show that the two curves coincide by recalculating

the accumbent potential from the field strength (Fig. 3). For

equal values of the field strength – not the potential - equal

effects are created, as we would expect according to the theory

of the Stark effect for hydrogen. Disturbance effects caused

by parasitic charged particles, as with photoelectrons, would

be dependent primarily on potential at these small pressures.

One can show further that the Ly_α - radiation for medium field

strengths (24 volts/cm) with differing H_2-pressures, decreases

with the hydrogen pressure. (Fig. 4.) The size of this ef-

fect resulting from the collision deactivation of the metasta-

ble atoms, can be calculated exactly, as we shall show. When

the short wave limit of the detector is displaced by the use

of a Ca F_2 window in place of the Li F window from 1050 to

1230Å, the fluorescence signal decreases with the absorption

in the D-bands below 1% of the normal signal. This residue

radiation cannot be influenced within the limit of error of

this special measurement (20%) by an electrical field.

On the other hand, before dissociation limit, the effective

average for the production of fluorescent radiation in the

Ca F_2 region (1230-1500 $\overset{o}{A}$) is considerably larger. Here, too,

the radiation intensity is independent of the existence of

an electrical field: The same is true for the fluorescence

measured before the dissociation limit in the LiF region

(1050-1500 $\overset{o}{A}$). Under certain experimental conditions, how-

ever, for the observed radiation in the Ca F_2 region, a field

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Fig. 2. Relationship of the Ly_α-intensity $I(Ly_\alpha)_F/I(Ly_\alpha)_o$

as a function of field strength.

Fig. 3. Relationship $I(Ly_\alpha)_F/I(Ly_\alpha)_o$ for two different

plate distances (+ and 0) of the quenching condensor

as a function of field strength. (-) curve calculated

according to equation (15).

Fig. 4. Relationship $I(Ly_\alpha)_{24}/I(Ly_\alpha)_o$ as a function of

hydrogen pressure in the measuring chamber. (-) curve

calculated according to equation (15).

dependency can be measured. Because this can not be a ques-
tion of Ly_α-radiation, therefore, a disturbance effect must
be the cause. One can show that this radiation is a result
of the photo-electrons sent through the field. The effect
disappears completely when grid electrodes of high output are
used as field electrodes and when the counter electrode is
made negative with respect to all limits of the measuring
chamber.

Discussion of Measurements

According to the previous discussion, in the case of the
observed fluorescence, we are dealing with Ly_α-radiation
of the H-atoms which arises through predissociation (1). The
hydrogen atoms receive from the dissociation process a definite
energy which is superimposed upon the half thermic energy of
the molecule before the dissociation as additional kinetic
energy. Since under experimental conditions in the field-free
case the life span of the metastable H-atoms is long compared
to the time between two impulses in the gas, through observa-
tion of the fluorescence the collision deactivation of the
excited particles can be measured. In addition, at first at
a constant H_2-pressure, the Ly_α-fluorescence is measured as
a function of the field strength of the quenching field. The
intensity of the radiation increases for decreasing vibration

quantum numbers; this means, the energy rich atoms are deacti-
vated the most by collisions. The measured effect arises from
the fact that, among other things, collision processes exist
through which metastable H-atoms are deactivated without
Ly -emission and thus disappear from the total emission. This,
in addition to other collision effects, a competition arises
between collision deactivation without radiation and spontan-
eous emission. By varying the H_2-pressure or varying the life
of the metastable particles, this competition can be changed
in favor of the one or the other effect.

In the field-free state, the life of the H(2S)-atoms is
limited by a two-quantum jump in the ground state to 1/7
second.[8.)] Although the transfer to the lower-lying $2P_{1/2}$-state
is possible through light radiation, the transfer probability
is a very small value because of the small size of the Lamb-
shift. Bethe gives the life expectancy of the particle with
respect to this decomposition as approximately 20 years. The
degeneration of the fine structure levels, which arises when
the radiation field is neglected, is nullified only very little
by the Lamb-shift and the fine structure. The wave function

8.)
    H. Bethe u. E. Salpeter Quantum Mechanics of One and Two-
    Electron Atoms. S. Flügge ed. Handb. Physik Bd. 35, S.
    372, Springer-Verlag. Berlin 1957

is greatly affected even by weak external fields. From the

pure configuration of 2S there arises under the influence of

the electrical field a mixed configuration of portions of

2S and 2P. For a weak field, in which the Stark-effect

splitting is very small with respect to the Lamb-shift, the

reciprocal life expectancy of the metastable state can be

calculated by using formula (4).
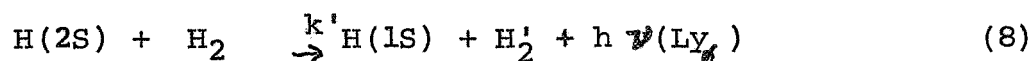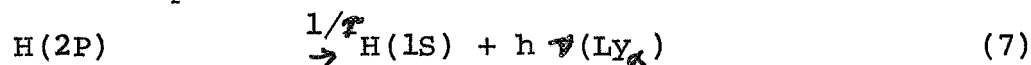
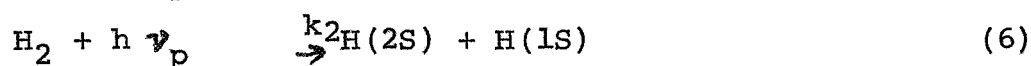$$1/\tau \ (F) \ = \ .2773 \cdot F^2 \ \left[sec^{-1}\right] \tag{4}$$
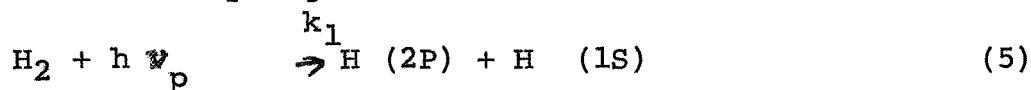
The life span of a H(2S) accordingly for a field of only 1 volt/cm
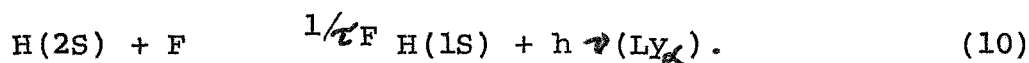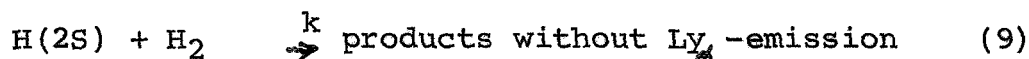
The field strangth F thereby is to be given in volt/cm, not

larger than Υ (1volt/cm) $\sim$ $3 \cdot 10^{-4}$ sec. By increasing the

field strength, the competition between collision processes

and spontaneous emission can thus be changed in favor of the

emission. Since the life expectancy can be given for each

field-strength value, the cross section for the competing

collision processes can also be calculated. In addition, the

dependency of this effective cross section can be determined

from the velocity of the H-atoms when the quenching curve is

obtained for particles of differing kinetic energy. Since the

impulse probability decreases when the H_2-pressure is lowered,

the quenchable portion in the radiation must increase, as

shown in fig. 4.

Although, at the applied H_2-pressures in the field-free

state, all metastable H-atoms within their life span reach a

collision, nevertheless, according to fig. 2 according to the

velocity of the particles, between 65 and 80% of the total

radiation is emitted. For this, two processes can come into

question. First, it is possible that both metastable H(2S)-

atoms and short-lived H(2P)-atoms, arise during pre-dissocia-

tion. The B-state, from which the decomposition results, has

the term symbol $1\Sigma_u^+$. Such a state results from the states of

the divided atoms $S_g + S_g$ and $S_g + P_u$. Considerations of

symmetry offer no information about which of the two cases,

or if perhaps both cases together, come into question for the

B'-state. The short-lived H(2P)-atoms ($\tau = 1.6 \cdot 10^{-9}$ sec.)

would not under our research conditions come to a state of

collision and could therefore be responsible for the radiation

at zero field strength. In addition, the collisions with H_2-

molecules are known, which lead to the quenching of metastable

atoms with resulting Ly_α-emission. Fite gives for particles

at a temperature of about $3000^\circ K$ an effective cross section

of $\overset{\bullet}{A}^2$ for this collision process.

According to the previous considerations, the following

reaction scheme can be set up for the origin and deactivation

of the excited hydrogen atoms:

$$H_2 + h\nu_p \xrightarrow{k_1} H(2P) + H(1S) \tag{5}$$

$$H_2 + h\nu_p \xrightarrow{k_2} H(2S) + H(1S) \tag{6}$$

$$H(2P) \xrightarrow{1/\tau} H(1S) + h\nu(Ly_\alpha) \tag{7}$$

$$H(2S) + H_2 \xrightarrow{k'} H(1S) + H_2' + h\nu(Ly_\alpha) \tag{8}$$

$$H(2S) + H_2 \xrightarrow{k} \text{products without } Ly_\alpha\text{-emission} \qquad (9)$$

$$H(2S) + F \xrightarrow{1/\tau_F} H(1S) + h\nu(Ly_\alpha). \qquad (10)$$

With the exception of a state of equilibrium for the concentration of the H(2S)-atoms, from all this we can derive formula (11) for the intensity of the Ly_α-radiation to be measured.

$$J_{Ly_\alpha}(F) = J(h\nu_p) \cdot [H_2] \left\{ k_1 + k_2 \left[\frac{k'[H_2]}{(k'+k)[H_2] + 1/\tau_F} \right. \right.$$

$$\left. \left. + \frac{1/\tau_F}{(k'+k)[H_2] + 1/\tau_F} \right] \right\}. \qquad (11)$$

According to the kinetic model, an equivalent formula can be derived in which the obvious values in the form v/λ appear in place of the products $k \cdot [H_2]$. v is the velocity of the impinging particles and λ is the mean free distance for the observed collision. Accordingly the probability for the occurance of the Ly_α-emission by collisions with metastable H-atoms is given by:

$$W = \int_0^\infty \left\{ \exp\left\{ -\frac{vt}{\lambda} \cdot \exp_{-\frac{t}{\tau_F}} \cdot \frac{v}{\lambda'} + \frac{1}{\tau_F} \left[\exp\left\{ -t(1/\tau_F + v/\lambda) \right\} \right] \right\} dt$$

$$= \frac{v/\lambda'}{(v/\lambda) + (1/\tau_F)} + \frac{1/\tau_F}{(v/\lambda + (1/\tau_F)}; \quad 1/\lambda = 1/\lambda' + 1/\lambda. \qquad (12)$$

λ and λ' are the mean free distances for the collisions of the kind described by (8) and (9). Since the collision cross sec= tions for the processes in (8) and (9) are larger than the gas-kinetic cross sections, we can use the velocity v of the particles resulting from the dissociation.

In fig. 2 the ordinate scale is given in units of

$$I_{LY\alpha}(F) \, / \, I_{LY\alpha}(0)$$

For $F = 0$, $1/\tau_F$ becomes small with respect to the expressions $k' \cdot [H_2]$ and $(k' + k \cdot [H_2])$. Thus (11) changes to

$$I_{LY\alpha}(0) = I(h\,\nu_p) \, [H_2] \left\{ k_1 + k_2 \, \frac{k'}{k' + k} \right\} . \qquad (13)$$

For the case of complete quenching of the metastable atoms by the field ($F > 150$ volt/cm) we get equation (14).

$$I_{LY\alpha}(F > 150) = I(h\,\nu_p) \, [H_2] \left\{ k_1 + k_2 \right) \qquad (14)$$

Equation (11) described the total Ly_α-radiation produced in the volume measured. The measured radiation is, however, still different from it. The multiplier sees only a portion P of the total radiation. In addition, the detection probability A of the detector is a function of radiation frequency v and incident angle α of the radiation. Furthermore, the atoms emit their radiation in the electrical field. As a result, the radiation distribution becomes anisotropic. If we begin with the plausible assumption that the radiation in the field-free case and the radiation induced by the collision are isotropic, then at a constant pressure for the radiation measured by the detector this expression results:

$$I_{LY\alpha}(F)_{gem} = \frac{1}{X} \, P \, A \, (\nu\,\alpha) \, I(h\,\nu_p) \, [H_2]$$

$$\left\{ k_1 + k_2 \left[\frac{X \cdot k' \, [H_2]}{(k' + k)[H_2] + 1/\tau_F} + \frac{1/\tau_F}{(k' + k)[H_2] + 1/\tau_F} \right. \right. . \qquad (15)$$

The factor X gives us the variation from isotropie. For the

applied pressure and the geometry of the measuring chamber,

the result for X = 1.2 is obtained with fair exactness.

The anisotropie of the Ly$_\alpha$-radiation emitted from the

H(2S)-atoms in weak electrical fields has been measured by

Fite and his coworkers.[10.)] Thus an earlier work by Lichten

is confirmed[11.)] which reported an isotropic distribution

under the assumption that only the $2P_{1/2}$-state participates

in the radiation. It could be demonstrated that through the

Stark-effect, also, the state $2P_{3/2}$ participates up to 10%.

In this way the radiation leading to the ground state is emit-

ted from both P-states. The expected polarization of the

radiation receives a value of -30% (the calculated value in

our paper: -32.9%). Of the anisotropic part of the radiation,

the detector observing in field direction sees a smaller por-

tion than with isotropic distribution. For an aperture angle

of 120°, the variation for the given gemoetry of the measur-

ing chamber and the applied H_2-pressure has the value 1/2.

from both quantities - polarization and geometry factor - we

calculate the anisotropie factor X = 1.2.

10.)
    W.L. Fite, W.E. Kauppila u. W.R. Ott, Phys. Rev. Let.

    20, 409 [1968].

11.)
    W. Lichten, Phys. Rev. Let. 6, 12 [1961].

Equation (15) was made the basis for the calculations

of effective cross section for the deactivating collision

processes. In addition, program GLSQ6 of the IBM 7090 Computer

(II M Bonn) was used. This program made it possible to deter-

mine the best curve consistant with the measured values ac-

cording to the method of the squares of least deviations.

The procedure includes the velocity constants k and k' and

the branching ratio V(2P/2S) into the atomic levels H(2P)

and H(2S) as parameters. The curves for the different primary

velocities of the H-atoms are given in fig. 2. Accordingly

we get the values in Table 1 for the parameters.

For the computation of quantities k, k' and V(2P/2S)

the measured values were used in the form

$$I_{Ly_\alpha}(F)_{gem} / I_{Ly_\alpha}(0)_{gem}$$

An explicit statement of the quantities A (v, α) and P is,

therefore, not necessary. With the calculation of the aniso-

tropie factor it was assumed, to be sure, that the sensitivity

of the detector is the same for all incident angles α. A

deviation from the assumption leads to a weak dependency of

the quantity X on A(v, α).

The best fit of the measured data is obtained with all

measurement curves for a separation ratio V=1/80. A 20% por-

tion of H(2P) in the total number of excited atoms is clearly

outside the error of measurement. The quality of the fit for

V=1/80 is a flat maximum. Accordingly, about 1% of the excited particles would be in the 2P-state. We conclude therefore from the experiments that within the limits of error with the predissociation according to (1), no short-lived, excited H-atoms are formed. This also indicates that the measured radiation comes exclusively from the Lyα- emission of the excited H-atoms, because each type of radiation of another wave length would behave in the data and calculations as non-quenchable radiation of the H(2P)-atoms.

Kolos and Wolniewicz have made calculations of the first excited H$_2$-state (B$^1\Sigma_u^+$) [12.)] They were able to show

v'	$h\nu_p$ eV	E eV H-Atom	$v \times 10^{-5}$ cm sec	$\bar{v} \times 10^9$ cm sec	$k \times_3 10^9$ cm^3 Molek.·sec	$k \times 10^9$ cm^3 Molek.·sec
Diss Grenze	14.676					
3	14.78	0.052	3.17	3.54	2.08	1.7
4	15.01	0.167	5.68	5.89	3.5	2.48
5	15.22	0.272	7.26	7.43	6.61	3.53

Table 1. Values of energy, velocity and velocity constants for H(2S)-atoms from the predissociation of the B-bands v'=3, 4 and 5.

that the wave function of the Heitler-London type 1 s t pσ, in

12.)
W. Kolos u. L. Wolniewicz, J. Chem. Phys. 45, 509 [1966].

which the one electron is in a ls-atomic orbital and the other

in a 2pσ, is of very great significance comparatively for

small and large nuclear distances. The overlapping integral

between the exact wave function and the l s 2 pσ - function

is for all nuclear distances larger than that with the l s

2 p-function. Since the state B' is orthogonal to the B-state,

one can conclude with approximate correctness from this that

in this case the l s 2 s-function assumes the roll of the

l s 2 pσ-function of the B-state. In the case of the separa-

ted atoms, we expect that for the B'-state the atoms are to

be found in the lS and 2S states as is shown also by our

experiment. In an analysis of the dissociation behavior of

Tydberg-levels of the hydrogen molecule, this is confirmed
by Mulliken.[13.)]

The evaluation of the quenching curves of fig. 2

with the help of equation (15) leads to the energy dependency

of the equilibrium constants as presented in fig. 5. Listed

are the quantities which according to equation (16)

$$k = \sigma v \tag{16}$$

represent the effective cross section of the processes divided

13.)

R. S. Mulliken, J. Am. Chem. Soc. 88, 1849 [1966]

by the particle velocity v: While the collision in the

region of measurement taking place without Ly$_\alpha$ -radiation

remains independent of the energy, the effective cross sec-

tion for process (8) increases with increasing particle velo-

city v. The quenching curves not only for the absorption of

the primary radiation in the oscillation bands v = 3, 4 and 5

of the D-state were obtained, but also for bands v' = 6 and 7,

the two lying above ionization limit. The values of the velo-

city constants determined for this have been corrected before

their listing in fig. 5. A comparison of the ionization and

absorption cross sections shows namely that for the absorbed

primary wave=length at v' = 6 and 7 a small portion of the

ultraviolet light leads to ion-formation of approximately the

same intensity. The photo-electrons formed by this photo-

ionization are accelerated by this applied quenching field

and produce through collision a small additional Ly$_\alpha$-intensity.

from the quenching curves are thus derived the values k and k'

which are somewhat too large. They were therefore not

included in the table of values (1). If we extrapolate the

curve for the energy dependency of k/v and k'/v for higher

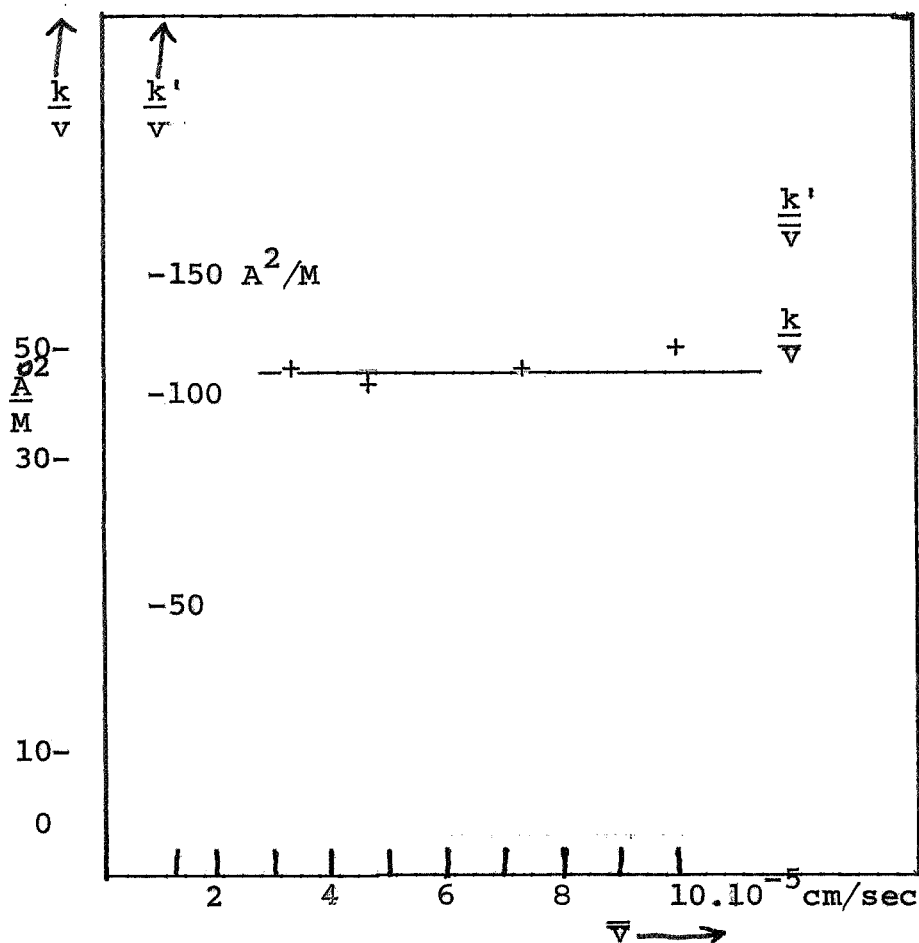energies and fit the values obtained from the quenching curve

Fig. 5. Cross section of the two collision processes (8) and (9) as function of the mean particle velocity v.

for v' = 6 onto this curve, then the values for the effective

cross section for v' = 7 lie exactly on these curves, as

can be seen in fig. 5. Even though the exact values for the

collision deactivation of H(2S)-atoms can not be obtained

experimentally from the vibration states v' = 6 and 7, never-

theless they indicate the qualitative course for the energy

dependency of the values k/v and k'/v.

The velocity constant k' describes the collision

excitation of the two (2P)-states of the H-atoms. The level

intervals of $2P_{3/2}$ and $2P_{1/2}$ to $2S_{1/2}$ are very small and

equal only 10^{-3} _viz._ 10^{-4} times the thermic energy. For col-

lisions with protons, the effective cross sections have al-

ready been calculated.[14.)] The effective cross section is a

decreasing function of the relative energy. For H_2-molecules

as collision partners no calculations have been made as yet.

At room temperature the impinging molecules are not all in their

lowest energy level. Moreover, they are found predominantly in

their first excited rotation state. This rotation energy can,

however, not be changed into internal energy of the H-atoms.

In collision with the H-atoms, in addition to the 2P-excitation,

simultaneously a rotational excitation of the H_2-molecules can

occur. For collisions with unexcited H-atoms the effective

cross section for rotation excitation of H_2 have been calcula-

ted.[15.)] In the region of particle velocities of 3 to

7 $\cdot 10^{+5}$cm/sec the effective cross section increases rapidly

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14.)

    E. M. Purcell, Astrophys. J. 116, 457 1952 . - M. J.

    Seaton, Proc. Phys.Soc. London A68, 457 [1955].

15.)

    R. J. W. Henry u. A. Dulgarno, Proc. Phys. Phys. Soc.

    London 88, 611 [1966].

with increasing velocity and assumes values up to $7\overset{o}{A}^2$. Since

the radius of the Bohr orbit for n=2 is four times as large

as for the ground state, a correspondingly larger effective

cross section for collisions with H(2S)-atoms is expected.

For the considered collision process comparative values are

available. Fite and coworkers have measured for H(2S)-atoms

from a thermic velocity distribution of $3000^{o}K$ the effective

cross section of collisions with H_2-molecules at room tempera-

tures at $70\overset{o}{A}^2$.[9] We compare this value with a cross section

of $95 \overset{o}{A}^2$, the result of the measurements under discussion

here. For metastable H-atoms of 15 keV energy, Sellin gives

a cross section of $10 \overset{o}{A}^2$ for the same process.[16]

Collisions of metastable H-atoms with H_2 which occur

without emission of Ly$_\alpha$ have not as yet been calculated or

measured with certainty. With the H_3^+ -formation, however,

very recently the participation of excited H-atoms was required.[17]

Under experimental conditions, because of the short length of

life of the 2P-atoms, the participation of metastable H-atoms

was assumed to be probable. Whether or not in the H_3^+ -formation

16.)
    I. A. Sellin, Phys. Rev. 136, A 1245 [1964].

17.)
    W. A. Chupka, M.E. Russell u. K Refaey, J. Chem. Phys.
    48, 1518 [1968].

atoms actually participate must be checked at higher resolu-
tion powers. According to Chupka's findings the possible ef-
fective cross section for the formation of molecular ions
from the collision of excited H-atoms with H_2 is said to be
in the order of $10^{-16} cm^2$ and to be a decreasing function of the
velocity of the atoms ($\sim 1/v$).   Quenching experiments,
which might have given an indication of the primary partners
in the reaction to form H_3^+-ions, took place without success.
From our own experiments it was concluded[2] that the chemical
ionization to H_3^+ takes place for the most part as the result
of collisions with excited molecules. The estimated small
participation of H-atoms in the reaction can be deceptive
because of the applied high H_2-pressure (up to 0.6 Torr),
since in the maxima of the absorption curve, total absorption
already exists. According to the result of our measurements
it is clear that the collision processes not causing Ly_α-
emission (9) is independent of the kinetic energy of the H-atoms.
With good exactness the effective cross section as a function
of the kinetic energy has a constant value of $50 \mathring{A}^2$. It is
thus very much larger than it should seem to be from Chupkas
study[17.)   In this connection for the H_3^+ from H* the

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17.)
    W. A. Chupka, M. E. Russell u. K. Refaey, J. Chem. Phys.

    48, 1518 1968 .

intermediaty formation of an excited H_3 molecule has been sug-

gested which changes through auto-ionization into the into the

ion H_3^+. Because of the high energy of the linear configura-

tion, such collisions of the H-atoms are regarded as being reac-

tive, which strike the molecule vertically to the joining axis

in order to make possible the stable triangular configuration.

From a consideration of the potential curves for this, a cri-

tical approximation of the reaction partner is required at

1.3$\overset{o}{A}$. When the discovered collision process (9) leads to H_3^+,

because of the large effective cross section of 20$\overset{o}{A}{}^2$, a dif-

ference between end-on or side-on collisions make little

sence. Moreover, it turns out that every collision is effec-

tive. In a combined measurement of H_3^+-formation and Ly --

emission in weak electrical fields with a line width of the

exciting radiation of 0.2 $\overset{o}{A}$,we certainly ought to be able to

answer this question unequivically.

About the reactability of excited H-atoms little is

known. Likewise, except for the mentioned ones, no experimental

or theoretical results about the energy dependency of ion

formation on chemical ionization exist. In various photo-

chemical experiments,reaction between H(2P)-atoms and N_2 and

of definable energy. The investigation of collision deactiva-
tion with helium atoms as collision partners should produce,
in addition, an insight into the problem of the rotational
excitation of the H_2-molecule, since the He-atom can take up
no internal energy from the collision process. Experiments
of this type are being prepared.